

The present invention relates to new metal powder compositions. More specifically, the invention concerns a new iron-based powder which is useful for the preparation of soft magnetic materials having improved properties when used both at high and low frequencies. The invention also concerns a method for the manufacturing of soft magnetic composite materials prepared therefrom.

Soft magnetic materials are used for applications, such as core materials in inductors, stators and rotors for electrical machines, actuators, sensors and transformer cores. Traditionally, soft magnetic cores, such as rotors and stators in electric machines, are made of stacked steel laminates. Soft Magnetic Composite, SMC, materials are based on soft magnetic particles, usually iron-based, with an electrically insulating coating on each particle. By compacting the insulated particles optionally together with lubricants and/or binders using the traditionally powder metallurgy process, the SMC parts are obtained. By using this powder metallurgical technique it is possible to produce materials having a higher degree of freedom in the design of the SMC component than by using the steel laminates as the SMC material can carry a three dimensional magnetic flux and as three dimensional shapes can be obtained by the compaction process.

Research in the powder-metallurgical manufacture of magnetic core components using coated iron-based powders has been directed to the development of iron powder compositions that enhance certain physical and magnetic properties without detrimentally affecting other properties of the final component. Desired component properties include e.g. a high permeability through an extended frequency range, low core losses, high saturation induction, and high strength. Normally an increased density of the component enhances all of these properties provided that a sufficient electrical resistivity can be maintained. The desired powder properties include suitability for compression moulding techniques, which i.e. means that the powder can be easily moulded to a high density component, which can be

SUMMARY OF INVENTION.

The present invention concerns a new ferromagnetic powder composition, which is suitable of compaction to high density composite components. More specifically the present invention concerns a powder composition comprising soft magnetic iron or iron-based core particles, the surface of which are surrounded by an electrically insulating inorganic coating and which composition also includes a lubricating amount of silanes, titanates, aluminates, or zirconates.

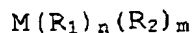
The present invention also includes a method of preparing high-density green, and optionally heat-treated, compacts from these compositions. This method comprises the steps of providing the composition, optionally mixing said composition with additives, such as conventional lubricants (i.e. particular lubricants) and binders as well as flow-enhancing agents; uniaxially compacting in a die at high pressure and ejecting the green body, which may subsequently be heat-treated.

Detailed description of the invention

The ferromagnetic powders used herein are made up of iron or an alloy containing iron optionally in combination with up to 20 % by weight of one or more of element selected from the group consisting of aluminium, silicon, chromium, niobium, molybdenum, nickel and cobalt. Preferably the new powder is based on a base powder that consists of essentially pure iron. This powder could be e.g. commercially available water-atomised or gas-atomised iron powders or reduced iron powders, such as

sponge iron powders. The powder particle shape could be round, irregular or flat.

Preferred electrically insulating coatings, which may be used according to the invention, are thin phosphorous containing coatings of the type described in the US patent 6348265 which is hereby incorporated by reference. Also other, preferably inorganic coatings may be used, for example coatings based on Cr, Mg, Mo, Zn, Ni, or Co. The lubricating agent used according to the invention is a type of organo-silanes, organo-titanates, organo-aluminates or organo-zirconates. This class of substances is often referred to as surface modifying agents, coupling agents, or cross-linking agents depending on the chemical functionality of their linked groups. The specific type of organo-silanes, organo-titanates, organo-aluminates or organo-zirconates which are used according to the present invention and which may be referred to as organo-metallic compounds are distinguished by the presence of at least one hydrolysable group and at least one lubricating organic moiety. This type of compounds can be defined by the following general formula:



,wherein M is a central atom selected from Si, Ti, Al, and Zr; R_1 is a hydrolysable group; R_2 is a group consisting of a lubricating organic moiety; wherein the sum of $m+n$ must equal the coordination number of the central atom and where n is an integer ≥ 1 and m is an integer ≥ 1 .

Particularly R_1 is an alkoxy group having less than 12 C atoms. Preferred are those alkoxy groups, which have less than 6, and most preferred are alkoxy groups having 1-3 C

atoms. R_1 may also be a chelate group, such as a residue of hydroxyacetic acid ($-\text{OC}(\text{O})-\text{CH}_2\text{O}-$) or a residue of ethylene glycol ($-\text{OCH}_2\text{CH}_2\text{O}-$).

R_2 is an organic group including between 6-30, preferably 10-24 carbon atoms optionally including one or more hetero atoms selected from the group consisting of N, O, S and P. R_2 is a group consisting of an organic moiety, which is not easily hydrolysed and often lipophilic and can be a chain of an alkyl, ether, ester, phospho-alkyl, phospho-alkyl, phospho-lipid, or phospho-amine. The phosphorous may be present as phosphato, pyrophosphato, or phosphito groups. Furthermore, R_2 may be linear, branched, cyclic, or aromatic.

A preferred group of lubricating silanes according to the present invention are alkyl-alkoxy silanes and polyether-alkoxy silanes. Furthermore, promising results have been obtained with hexadecyl-trimethoxy silane, isopropyl-triisostearyl titanate, isopropyl-tri(dioctyl)phosphato titanate, neopentyl(diallyl)oxy-tri(dioctyl)phosphato zirconate, neopentyl(diallyl)oxy-trineodecanoyl zirconate, and diisobutyl-acetoacetyl aluminate.

The amount of the compound is preferably present in amounts above 0.05%, such as in amounts of 0.05-0.5%, preferably 0.07-0.45%, and most preferably 0.08-0.4% by weight of the composition. A too low amount of lubricating agent gives high density but results in poor ejection behaviour and may thus result in poor surface condition of the tool and/or SMC parts. A too high amount, however, may give excellent ejection behaviour but could render in low component densities. Furthermore it is preferred that the compound is present as a lubricating layer on the insulated particles. It should,

however, be noted that the geometry of the component as well as the material and quality of the tool, have great impact on the surface condition of the SMC parts after ejection.

5 The use of compounds organo-silanes, organo-titanates, or organo-aluminates is known from US patents 4820338 and 6537389. According to the US patent 4820338 silanes, titanates or aluminates are used in order to accelerate a coupling between the magnetic powder particles and an
10 electrically insulating organic binder polymer. The powder particles do not have an inorganic coating.

The US patent 6537389 discloses a wide range of silicon-, aluminium-, or boron-containing compounds as molecular
15 precursors for producing electrically insulating ceramics on soft magnetic powders. The precursor compounds are converted by thermal treatments into ceramic, metallic or intermetallic end products to enhance temperature and solvent resistance. The US patent 6537389 distinguishes
20 from the present invention i.a. in that the organo-metallic compounds are used as precursors for producing chemically and thermally resistant coatings, and not as the key component that facilitates production of high density parts. Furthermore, the precursor compounds
25 described in the examples of US patent 6537389 do not include a lubricating moiety.

The lubricating compound(s) used according to the present invention can be used in such a way that it is dissolved or dispersed in a suitable solvent, e.g. an organic sol-
30 vent, such as acetone or ethanol. The obtained solution or dispersion is subsequently added to the iron based powder during mixing and optionally heating. The solvent is finally evaporated optionally in vacuum.

10 The term "essentially consisting" is intended to mean
that at least 40 %, preferably at least 60 % of the
particles have a particle size above 106 and 212 μm ,
respectively. So far the best results have been obtained
with powders having an average particle size about 250 μm
15 and only less than 3 % below 106 μm . The maximum particle
size may be about 5 mm. The particle size distribution
for iron-based powders used at PM manufacturing is
normally distributed with a Gaussian distribution with an
average particle diameter in the region of 30 to 100 μm
20 and about 10-30% less than 45 μm . Iron based powders
essentially free from fine particles may be obtained by
removing the finer fractions of the powder or by
manufacturing a powder having the desired particle size
distribution.

25 According to a preferred embodiment of the invention and
contrary to common practise in powder metallurgy, where
conventional PM lubricants are used in the iron powder
mix, or where a lubricant is used in combination with
binder and/or surface treatments the iron or iron-based
30 powder must not be mixed with a separate (particular)
lubricant before it is transferred to the die. Nor is it
necessary to use external lubrication (die wall

lubrication) where the walls of the die are provided with a lubricant before the compaction is performed. The invention, however, does not exclude the possibility of, when it is of interest, to utilise conventional internal lubrication (in an amount up to 0.5% by weight), external lubrication or a combination of both. The powder to be compacted may also include additives selected from the group consisting of binders, lubricants, and flow-enhancing agents. Examples of inorganic lubricants, which may be used in addition to organic PM lubricants, are hexagonal boron nitride, and MoS_2 .

According to the present invention soft magnetic composite materials having a density of at least 7.45 g/cm^3 can be prepared by uniaxially compacting the new powder compositions in a die at high compaction pressures and without die wall lubrication. When the green body has been ejected from the compaction tool it can be heat treated up to temperatures of about 700°C .

The term "at high compaction pressure" is intended to mean at pressures of about at least 800 MPa. More interesting results are obtained with higher pressures such as pressures above 900, more preferably above 1000, and most preferably above 1100 MPa. Conventional compaction at high pressures, i.e. pressures above about 800 MPa, with conventionally used powders including finer particles are generally considered unsuitable due to the high forces required in order to eject the compacts from the die, the accompanying high wear of the die, and the fact that the surfaces of the components tend to be less shiny or deteriorated. High electrical resistance can be obtained even though high compaction pressures are used to achieve the high density. By using the powders according to the pre-

The heat treatment may be performed at the temperatures normally used, e.g. up to temperatures of about 700°C in different types of atmospheres or at reduced pressure and optionally in the presence of steam. Prior to the heat treatment the pressed components may optionally be green machined and/or cleaned.

[illegible]

In brief the advantage obtained by using the powder and method according to the present invention is that high-density SMC parts can be cost-efficiently produced. SMC parts with remarkably high magnetic induction levels together with low core losses can be obtained. Other advantages are that the mechanical strength after heat treatment is increased and that, in spite of very high densities, compacted parts with high electrical resistance can be successfully ejected from the dies without negatively influence the finish of the die walls and/or on the surfaces of the compacted SMC parts. It is thus possible to obtain parts having excellent surface finish. These results can be obtained with a single compaction step. Examples of products of special interest for the new powder compacts are inductors,

The invention is further illustrated by the following examples. It is understood that the present invention is not limited thereto.

EXAMPLE 1

An iron-based water atomised powder (Somaloy 550™, available from Höganäs AB, Sweden) was used as starting material. This powder has an average particle size between 212 and 425 µm and less than 5% of the particles have a particle size below 45 µm. This powder, which is a pure iron powder, the particles of which are electrically insulated by a thin phosphorus containing barrier, was treated with 0.2% by weight of a hexadecyl-trimethoxy silane as a lubricating agent. The addition of the lubricating agent was performed as follows: hexadecyl-trimethoxy silane was diluted in ethanol to a 20% solution by weight and the solution was stirred during 60 minutes. An amount of this solution corresponding to 0.2% by weight was added during mixing to the iron powder, which had previously been heated to 75°C in the mixer. An intensive mixing was carried out in the same mixer during 3 minutes followed by mixing at a lower speed during 30 minutes and during vacuum in order to evaporate the solvent. A corresponding powder mixed with a conventional lubricant was used as comparison. This powder was mixed with Kenuolube™ before the compaction. The amount of the lubricant used was 0.5% of the composition, which is generally considered as a low amount of lubricant for components compacted at high pressures.

Rings with an inner diameter of 47 mm and an outer diameter of 55 mm and a height of 4 mm were uniaxially compacted in a single step at different compaction pressures 800, 1000 and 1200 MPa, respectively. Despite
5 the low amount of the organo-metallic lubricating agent and high compaction pressures the surfaces of the components showed no sign of deterioration.

After compaction the parts were heat treated at 500 °C for 30 minutes in air. The obtained heat-treated rings
10 were wound with 25 sense and 112 drive turns. The magnetic properties were measured in an LDJ 3500 Hysteresigraph. Table 1 summarizes the maximum relative permeability and the magnetic induction at 1500 and 6900 A/m respectively, measured under DC conditions. The core
15 loss/cycle has also been measured at 1 T and at 50 Hz and at 400 Hz, respectively.

The following table 1 demonstrates the obtained results:

Table 1

Sample	Compaction Pressure MPa	Density g/cm ³	μ_{max}	B_{1500} (T)	B_{5900} (T)	Core loss/cycle at 1T and 50 Hz (J/kg)	Core loss/cycle at 1T and 400 Hz (J/kg)
According to the invention	800	7.45	720	1.08	1.53	0.134	0.178
	1000	7.59	790	1.15	1.59	0.126	0.163
	1200	7.64	820	1.18	1.62	0.124	0.165
Comparative example	800	7.39	620	0.95	1.46	0.142	0.200
	1000	7.47	590	0.95	1.49	0.140	0.198
	1200	7.49	550	0.92	1.48	0.140	0.193

As can be seen from table 1 the green density is significantly higher for the powder according to the invention and magnetic properties are, hence, improved compared with the materials used in the comparative examples. The comparative example also demonstrates that no or only minor improvements of the magnetic properties can be obtained by increasing the compaction pressure to 1000 MPa and 1200 MPa.

Despite the obtained high density of the samples the core losses are maintained at a low level even at 400 Hz,

TABLE 2

Amount of silane	Green density (g/cm ³)	Relative Ejection Energy %	Surface finish
0%	7.66	100	Seizure
0.1%	7.67	58	Good
0.2%	7.66	48	Good

10 From table 2 it can be seen that the energy needed for
ejection is considerably reduced and the surface finish
is improved by minor additions of an organo-metallic
lubricating agent according to the present invention. It
can also be observed that an increase from 0.1% to 0.2%
15 by weight of a lubricating agent has a positive impact on
the ejection energy.

EXAMPLE 3

This example demonstrates the effect of the chain length of the unhydrolysed group or groups (R_2) of the organo-metallic compound on the lubricating properties at ejection after compaction with high pressures. In this example various types and amounts of alkyl-alkoxy silanes (central atom Si) are used as lubricating agent. Two kinds of high purity water atomised iron-based powder provided with a thin insulating coating with two different particle size distributions were used to show the influence of the particle size. The S-powder has about 14 % of the particles less than 45 μm and a weight average particle size of about 100 μm . The C-powder has a

significantly coarser particle size distribution with a weight average size of about 250 μm and less than 3% below 106 μm .

- 5 Five different kinds of organo-silanes were used (A-E):
- A Methyl-trimethoxy silane
 - B Propyl-trimethoxy silane
 - C Octyl-trimethoxy silane
 - D Hexadecyl-trimethoxy silane
 - 10 E Polyethyleneether-trimethoxy silane with 10 ethylene ether groups

Five different alkyl-alkoxy silanes in the range 0.05 to 3.0% by weight were added to the insulated iron-based

15 powder and the obtained mixtures were compacted at 1100 MPa in a uniaxial press movement into slugs with a diameter of 25 mm and a height of 12 mm. During ejection the dynamic ejection force per unit sliding area was measured and after ejection green surface finish was

20 evaluated and density was measured as is shown below in table 3.

TABLE 3

	Powder C	Powder C	Powder C	Powder S	Powder C	Powder S	Powder C	Powder C
Silane	0,05%	0,1%	0,2%	0,2%	0,4%	0,4%	1,0%	3,0%
A								Seizure
B							Seizure	
C			Seizure		58 N/mm ² Poor 7,60 g/cm ³			
D	89 N/mm ² Poor 7,70 g/cm ³	69 N/mm ² OK 7,70 g/cm ³	38 N/mm ² OK 7,68 g/cm ³	63 N/mm ² Poor 7,65 g/cm ³	47 N/mm ² OK 7,57 g/cm ³	54 N/mm ² OK 7,54 g/cm ³		
E		80 N/mm ² Poor 7,70 g/cm ³	35 N/mm ² OK 7,69 g/cm ³	75 N/mm ² Poor 7,64 g/cm ³	32 N/mm ² OK 7,59 g/cm ³	49 N/mm ² OK 7,60 g/cm ³		

As can be seen from table 3 a chain length below 8 carbon atoms in the alkyl chain does not give satisfactory results, even though the added amount is high. Hence, at least 8 atoms in the lubricating (alkyl, or polyethyleneether,) chain group or groups are needed in order to successfully eject the component. An added amount above 0.5% is believed to be of less interest, as the density of the green component will be negatively

influenced. The table also shows, that when the organo-silane content is less than 0.05%, ejection without damaging the component and the surface of the die is not possible for the silane "D" that contains 16 atoms in the lubricating alkyl group. However, the geometry of the component as well as the quality of the tool have a great impact on the surface condition of the component after ejection. Therefore, lower amounts than 0.05% lubricant agent, optionally mixed with conventionally used i.e. particular lubricants, can be of interest for some applications.

From table 3 it can also be concluded that extremely high densities can be obtained. The coarse powder shows superior ejection behaviour compared to the standard powder. Even powder with a standard particle size distribution can be compacted to high density (about at least 7.60 g/cm³). As is noted above, the ejection behaviour is also here greatly dependent on component geometry and tool material and quality. Thus, powders with a standard size distribution can be of interest in some applications.

EXAMPLE 4

This example demonstrates the lubrication effect of organo-metallic compounds with different central atoms. In this example the lubrication effect of four different agents have been examined i.e. silane, titanate, zirconate and aluminate, having Si, Ti, Zr and Al as the central atom, respectively. The various central atoms have different coordination numbers and chemical properties. However, the chemical structure of the organo-metallic compound was selected so that the chain length of the lubricating group or groups (R₂) would show

A high purity water atomised iron-based powder with a thin insulating coating were treated with 0.2% by weight of each organo-metallic compound as lubricating agent.

Four different types of organo-metallic agents were examined (A-D);

- A Isopropyl-triisostearoyl titanate
B Neopentyl(diallyl)oxy-trineodecanonyl zirconate
C Diisobutyl(oleyl)aceto-acetyl aluminate
D Hexadecyl-trimethoxy silane

TABLE 4.

Organo-metallic compound	A	B	C	D
Ejection force [N/mm ²]	35	44	50	39
Denisty [g/cm ³]	7.68	7.68	7.68	7.68
Ejection and part quality	OK	OK	OK	OK

As can be seen from table 4 the lubricating properties of all compounds are satisfactory. Hence, the type of central atom shows only minor influence on the lubricating properties. The chain length, and to some extent the chemical structure, of the unhydrolysed group

The influence of average particle size and particle size distribution was further investigated. Three different high purity iron-based powders with different particle size distributions, according to table 5, all of them insulated with a thin phosphate-based electrical insulation were prepared. All samples were treated according to the present invention with 0.2 wt% of hexadecyl-trimethoxy silane according to the procedure described in Example 1.

Cylindrical samples with a diameter of 25 mm and a weight of 50 grams were compacted in an uniaxially press movement at a compaction pressure of 1000 MPa and green densities above 7.6 g/cm³ for all the samples were obtained.

TABLE 5

Particle size distribution	Sample A (%)	Sample B (%)	Sample C (%)
-45 μm	8.4	0.0	0.1
45-106 μm	52.7	15.5	1.0
106-212 μm	30.0	84.3	37.4
212-315 μm	0.1	0.2	51.0
+315 μm	0.1	0.0	10.5
Density [g/cm ³]	7,61	7,63	7,62
Surface finish	Poor*	OK	Good

* Higher amount of lubricant agent improves surface finish.

It could be observed that the surface finish of the sample C was superior to those of the samples A and B, respectively.

EXAMPLE 6

This example illustrates the importance of the inorganic insulation.

- 10 A high purity iron powder, the particles of which are electrically insulated by a thin phosphorus-containing barrier was compared with an identical powder without the phosphorous-based inorganic insulation. Both types of powders were subsequently treated with 0.2% by weight of

hexadecyl-trimethoxy silane as a lubricating agent according to the invention.

Rings with an inner diameter of 45 mm and an outer diameter of 55 mm and a height of 5 mm were uniaxially compacted in a single step at compaction pressure 1100 MPa. After compaction the parts were heat treated at 500°C for 30 minutes in air. The electrical resistivity was measured by the four-point method.

The following table 6 shows electrical resistivity and density of composite components prepared of powders with and without insulated particles.

TABLE 6

	Electrical Resistivity [pOhm*m]	Density [g/cm ³]
According to the invention	150	7,68
Comparative example	0,5	7,68